SORPTION PROPERTIES OF ZEOLITE Y MODIFIED BY CONTROLLED DEPOSITION OF INTRACRYSTALLINE COKE*

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The possibility of zeolite Y modification by controlled deposition of coke during the process of methanol conversion was studied. It was found that coke deposits lower the sorption capacity of the zeolite, which yields the possibility to obtain modified zeolite of definite sorption properties. The process of coking was analysed using the results of kinetic measurements, XRD, IR, TGA, and sorption-isotherms determination. The Polanyi–Dubinin potential theory was applied to describe the water–vapor sorption isotherms.

The term "coke" denotes carbonaceous residues which are deposited on catalysts during reactions in which carbon-containing species are involved. In petroleum refining and in petrochemistry, catalyst deactivation caused by the formation of carbonaceous deposits (coke) is one of the main technological and economic problems[1-4]. In recent years, considerable efforts were undertaken to achieve a more systematic understanding of the factors which are responsible for coke formation in the intracrystalline channels or on the external surface of zeolite crystals[5-8]. It is therefore particularly important to specify the kinetics and the mechanisms of the formation of the coke. Many experimental techniques can be employed for the characterization of carbonaceous residues[1]. Although a critical assessment of all these techniques is still lacking, it appears from some publications[9-13] that XRD, TGA, IR, kinetics, and sorption techniques are very powerful tools in this field.

In sorption investigations, the Polanyi–Dubinin (PD) potential theory[14,15] developed by Dubinin[16] as the theory of volume filling of micropores is particularly important. Its fundamental formula is the Dubinin–Radushkevich (DR) equation[14-16]:

$$W = W_0 \exp\left[-B\left(\frac{T}{\beta}\right)^2 \log^2\left(\frac{p_s}{p}\right)\right] = W_0 \exp\left[-k\left(\frac{A}{\beta}\right)^2\right], \qquad (1)$$

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where W represents the volume of the liquid-like adsorbate present in micropores at temperature T and at relative pressure p/p_s, W_0 is the total volume of the micropores, B and k are the structural parameters correlated with micropore dimensions, A is the differential molar work of adsorption, and β is the constant characterizing the adsorbate (the affinity coefficient).

Recently, the applicability of the PD theory to studies of sorption on zeolites was proven[13,17–21]. The literature, e.g. refs[5,6,12,22–28], is dealing mainly with catalytic effects, nature of coke deposits and/or methods suitable for suppressing of the coke formation. The coke, however, has not been used yet as a modifying agent in zeolites.

The aim of this work is to investigate the process of controlled deposition of coke as a possible method of modification of zeolite Y properties.

EXPERIMENTAL

Preparation of the Acid Form of Zeolite Y

The NaY zeolite was prepared according to the standard procedure[29] and then kept over the saturated NH_4Cl solution. It is fairly known that the deposition of coke occurs essentially at the acid sites of zeolites. To convert the starting material into the acid form, the following procedure was applied. NaY was placed in the 2M-NH_4NO_3 solution at the ratio of 1 g of zeolite to 20 cm^3 of the solution. The mixture was heated up to 358 K and kept at that temperature for 24 h while stirring. Next, the zeolite was filtered and washed thoroughly with water. When dried in air at 383 K, the zeolite (in the 2—3 mm bed) was calcined in the air stream in two steps: initially at 653 K for 3 h and then at 723 K for 2 h. After the calcination, the zeolite was exposed to water vapor for about 24 h, and then the ion-exchange procedure was repeated. Three ion-exchange and two calcination processes were applied altogether. As a result, the H NH_4NaY zeolite was obtained. Next, the material was granulated using the 0·4 mm sieve, dried in air at 383 K overnight and kept sealed.

Coke-Deposition Procedure

It seemed essential to use in every individual coke-deposition process the same, freshly prepared substrate. In this purpose, a day before carrying out the deposition, a portion of H NH_4NaY was calcined as described above to yield the H(95)NaY material, i.e. the zeolite in which 95% of sodium is replaced by hydrogen (the exchange degree was estimated separately by the standard technique of ammonia adsorption at 423 K). Immediately after the calcination, 2·000 g of the material was weighed (while limiting as much as possible its exposition to the air), and sealed in a container.

To carry out the coke-deposition process, the prepared H(95)NaY sample was placed in a shallow-bed flow reactor. Then, a helium stream (1 cm^3 s^{-1}) was employed, and at the same time, the reactor temperature was raised up to a definite value. When the desired temperature was reached, a mixture of helium and methanol was applied with the helium flow rate as before and methanol–vapor flow rate of 0·5 g h^{-1} per 1 g of the zeolite sample. The mixture was accomplished by the injection of liquid methanol (in 1 . 10^{-3} cm^3 increments) into the stream of helium. After a definite period of time, the injection of methanol was terminated and the zeolite was purged with pure helium for about 1 h. Then, the sample was cooled down and sealed in a container. The process of coking was examined at 373, 423, 473, 523, 553, 593, 623, 653, and 673 K, respectively.

Methods

Kinetics of the coking process was studied using the modified procedure of Bibby et al.[6]. The 50 mg samples were taken out of the reactor at certain time intervals in order to determine changes in water–vapor adsorption and coke content. Before a sample was taken, the injection of methanol was stopped and the zeolite bed was purged with pure helium for about 20 min, to exclude from the reactor gaseous products of the methanol conversion. The sample was then quickly transferred into a weighed quartz container equipped with a Teflon stopper. After the sample was taken, the flow of helium and methanol vapor over the zeolite bed was resumed with the rate corrected for the decrease of the zeolite mass. When weighed, the sample was held over the saturated NH_4Cl solution at 298·2 K for 24 h, and then weighed again. Next, the sample was calcined at 823 K for ca 5 h in oxygen stream, and weighed once again. Thus, the water–vapor adsorption at a relative humidity of 79% and the amount of coke deposits in 1 g of pure dry zeolite could be calculated for each sample taken during the coke-deposition process.

X-Ray diffraction (XRD) *measurements* were performed within the range of $2\theta = 5 - 50°$ using silicon powder as an internal standard and CuKα radiation with Ni filter. The scanning was performed at the 0·02° steps. Approximately 15 reflections were used to calculate unit cell parameters by a least-squares fit to the interplanar spacings.

IR *spectra* were recorded within the range of 1 200 – 1 700 cm^{-1} using the conventional KBr technique.

Thermogravimetric analyses (TGA) were carried out on 200 mg samples in the flowing air atmosphere within the temperature range of 295 – 1 273 K and at the heating rate of 5 K min^{-1}.

Adsorption isotherms for water vapor were determined at 298·2 K in a vacuum device equipped with a McBain balance. The pressure within the range of $1 . 10^{-2} - 1 . 10$ Pa was measured with a "Baratron" vacuummeter. The pressure at higher ranges was determined with a resistance and differential vacuummeters. Before the adsorption measurements were begun, the samples were heated at 700 K under the stationary vacuum of approximately 10^{-3} Pa to a constant mass (for about 8 h).

RESULTS AND DISCUSSION

The amounts of coke deposits and water–vapor adsorption at 79% relative humidity determined for different coking temperatures, are presented in Figs 1 and 2 as functions of the amount of methanol passed over the zeolite. The results, which reflect the kinetics of coke formation in the samples studied, lead to the following concluions:

a) Obviously, the rate of the coke formation depends on both the reaction temperature and the amount of methanol applied (see Fig. 1).

b) Up to 473 K, the formation of coke deposits has not been noticed.

c) Within the range of 523 – 593 K, the mass of methanol used for conversion affects the amount of formed coke more strongly than the reaction temperature.

Above approximately 3 g of methanol per 1 g of zeolite, the amount of the coke formed becomes constant (26 – 28 wt. %). Since the formation of coke occurs presumably mainly at the active sites of zeolite, the plateau observed in Fig. 1 suggests complete filling of the zeolite pores with the deposits.

d) Above 593 K, the coke content increases steadily as with the mass of methanol as with the coking temperature. This fact indicates that, at higher temperatures, the process of coking also occurs intensively on the external surface of the zeolite crystals. Thus, the amount ratio of intercrystalline (external) to intracrystalline (internal) deposits increases with the reaction temperature.

e) The coking temperature does not influence the final effect of blocking the sorption spaces of the zeolite (see Fig. 2).

f) The effect of blocking the zeolite pores by coke deposits is limited: water–vapor adsorption is still about 10% for all the fully coked samples (the adsorption for the parent H(95)NaY is 31·5%).

In Table I, there are presented unit cell parameters obtained from the XRD measurements for samples treated with methanol at different temperatures. For the temperatures up to 473 K, the unit cell parameter is close to that of the non-treated zeolite. This fact agrees with the results of determination of coke content and of IR measurements (see Fig. 3) from which it is evident that coking does not occur up to 473 K. For the temperature range of 523 – 593 K, the unit cell parameter is higher by about 0·01 nm and, above 593 K, it increases with the reaction temperature. That observation points out that coke formed at 593 K and below that temperature influences the zeolite lattice in different way than that formed above 593 K, so, probably, different kinds of coke deposits form within the two temperature ranges.

This conclusion is confirmed by the IR difference spectra presented in Fig. 3 within the range of 1 200 – 1 700 cm^{-1}. These spectra were obtained by subtracting

TABLE I

Unit cell parameters for H(95)NaY treated with methanol at different temperatures

T_{tr}, K	a, nm	T_{tr}, K	a, nm
–[a]	2·4620	553	2·4723
373	2·4625	573	2·4709
423	2·4624	593	2·4719
473	2·4621	623	2·4751
523	2·4725	653	2·4777

[a] Parent sample.

the spectrum of the non-coked zeolite from those of the coked samples. According to the literature[30], the band at 1 590 cm^{-1} can be assigned to polycyclic aromatic compounds. The band occurs for all the samples obtained at temperatures starting from 523 K. The band at 1 540 cm^{-1}, occurring for the samples obtained within the range of 523 – 593 K, corresponds presumably to alkylnaphthalenes and/or polyphenylene structures[10]. The presented spectra show that the fraction of polyaromatic compounds increases with the temperature of coking while the fraction of aliphatic compounds decreases.

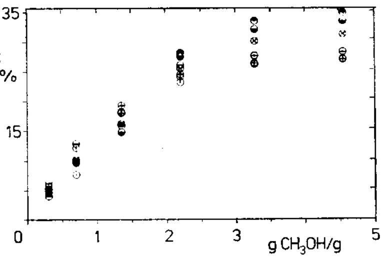

Fig. 1

Amount of coke formed on H(95)NaY (α, wt. %) as a function of the amount of methanol vapor in the stream of helium (g CH_3OH per g zeolite) in dependence on coking temperature (K): ⊙ 523, ⊖ 553, ⦶ 573, ⊕ 593, ⊗ 623, ◒ 653, ◓ 673

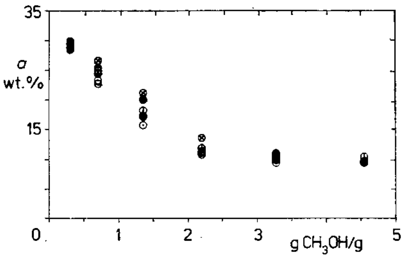

Fig. 2

Water-vapor adsorption at $p/p_s = 0{\cdot}79$ and $T = 298{\cdot}2$ K (a, wt. %) for coked H(95)NaY as a function of the amount of methanol vapor in the stream of helium (g CH_3OH per g zeolite) in dependence on coking temperature (K): ⊙ 523, ⊖ 553, ⦶ 573, ⊕ 593, ⊗ 623, ◒ 653, ◓ 673

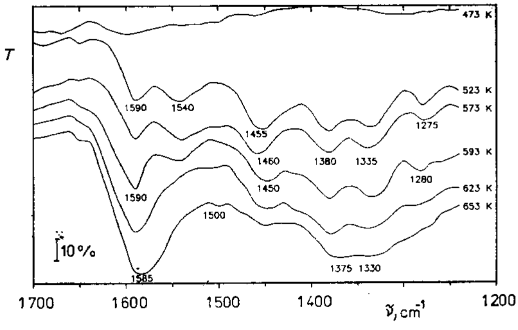

Fig. 3

IR difference spectra for H(95)NaY coked at different temperatures

Coke contents obtained from the TG curves (Fig. 4) confirm the data received from the calcination (see Fig. 1). The DTG curves (Fig. 5), however, reveal two peaks for the samples coked at 523 – 573 K: one peak within the temperature range of 573 – 673 K, and the other at 673 – 873 K. The former peak is probably connected, among other things, with the diffusion to and detachment from the zeolite-crystal surface of some, more volatile, coke deposits. The latter one, characteristic also for the samples coked at temperatures above 573 K, results mainly from the burning of coke.

Isotherms of water–vapor adsorption on the samples studied are presented in Fig. 6. The applicability of the DR equation (Eq. (*1*)) for the description of these isotherms is supported by the values of the determination coefficient (DC), listed in Table II. The determination coefficient is defined by the following expression[31]:

$$DC = r^2 = 1 - \sum_{i=1}^{N} (y_i - \hat{y}_i)^2 / \sum_{i=1}^{N} (y_i - \bar{y})^2 , \qquad (2)$$

where r is the correlation coefficient, y_i is the dependent variable, $\hat{y}_i$ is the value of the dependent variable approximated by the least-squares method, $\bar{y}$ is the

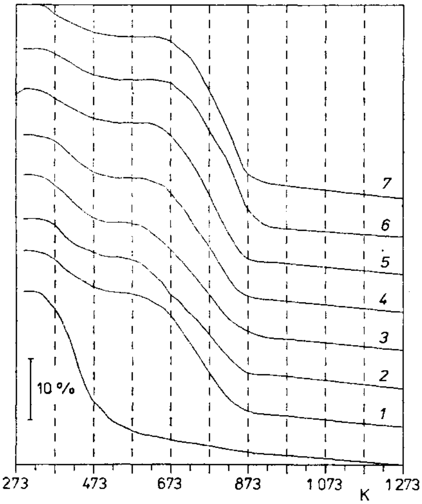

FIG. 4

TG curves for H(95)NaY coked at different temperatures. The bottom curve corresponds to the parent sample. Temperature of coking, K: *1* 523, *2* 553, *3* 573, *4* 593, *5* 623, *6* 653, *7* 673

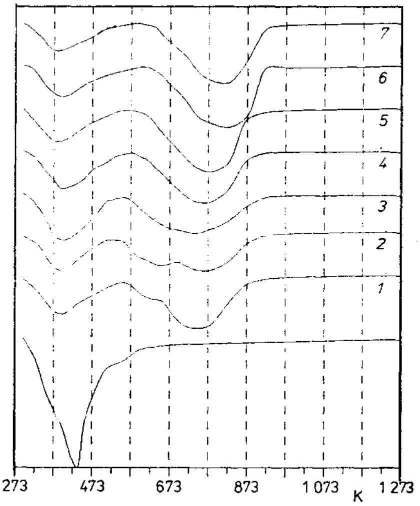

FIG. 5

DTG curves for H(95)NaY coked at different temperatures. The bottom curve corresponds to the parent sample. Temperature of coking, K: *1* 523, *2* 553, *3* 573, *4* 593, *5* 623, *6* 653, *7* 673 arithmetic mean value of the dependent variable, and N is the number of pairs of experimental data.

The values of the parameter W_0, obtained from Eq. (*1*), also demonstrate that the DR equation is applicable to the description of isotherms of water-vapor adsorption on the samples under study. These values, which characterize the volume of sorption spaces, agree with water–vapor sorption capacities, obtained from independent direct measurements of adsorption. The values of W_0 and sorption capacities are listed in Table II.

TABLE II

The determination coefficients (DC) and parameters of the Dubinin-Radushkevich equation (Eq. (*1*)), obtained from water-vapor adsorption isotherms at 298·2 K for H(95)NaY coked at different temperatures, and water–vapor sorption capacities recieved from independent measurements of adsorption for the same samples at p/p_s = 0·79 and T = 298·2 K

T K	DC	$k \,.\, 10^2$ $mol^2\,kJ^{-2}$	W_0 $dm^3\,kg^{-1}$	H_2O sorption capacity $dm^3\,kg^{-1}$
—[a]	0·9952	0·4932	0·3195	0·3150
523	0·9952	0·3929	0·0774	0·0775
573	0·9915	0·4110	0·0835	0·0785
593	0·9737	0·4527	0·0886	0·0845
623	0·9650	0·4478	0·0681	0·0792
673	0·9176	0·5968	0·0714	0·0708

[a] Parent sample.

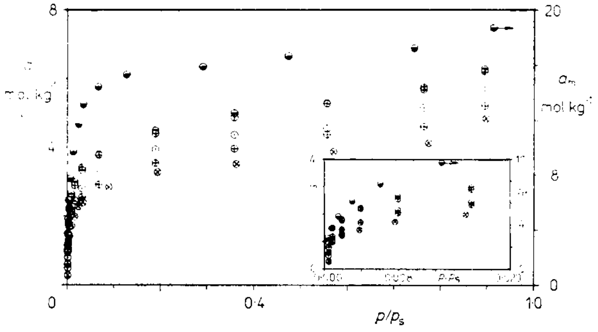

FIG. 6

Water–vapor adsorption isotherms at 298·2 K for H(95)NaY coked at different temperatures (K): ⊙ 523, ○ 573, ○ 593, ○ 623, ○ 673, ○ parent sample. The right axis relates to the parent sample

According to the PD theory, sorption is determined by the adsorption potential. As inferred from refs[13,21,32,33], the adsorption potential distribution is closely connected with the heterogeneity of microporous adsorbents. The distribution function, $X(A)$, is of the following form:

$$X(A) = -\frac{\mathrm{d}W}{\mathrm{d}A} = \frac{2W_0kA}{\beta^2}\exp\left[-k\left(\frac{A}{\beta}\right)^2\right], \tag{3}$$

where the symbols are the same as in Eq. (*1*). The course of $X(A)$ calculated from Eq. (*3*) for the samples under study is shown in Fig. 7. The maximum values of X, X_{max}, and the corresponding values of A, $A(X_{\mathrm{max}})$, are listed in Table III. The main finding which results from Fig. 7 and Table III is that X_{max} for the coked zeolite Y is considerably lower than that for the non-coked sample.

TABLE III

Characteristics of the function of the adsorption potential distribution for H(95)NaY coked at different temperatures

T K	$X_{\mathrm{max}} \cdot 10^3$ mol cm^3 kJ^{-1} kg^{-1}	$A(X_{\mathrm{max}})$ kJ mol^{-1}
–[a]	19·2	10·10
523	4·2	11·34
573	4·6	11·11
593	5·1	10·53
623	3·9	10·59
673	4·7	9·17

[a] Parent sample.

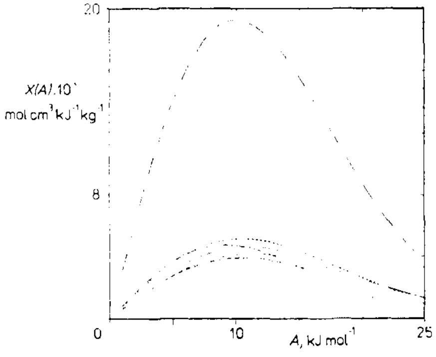

FIG. 7

The distribution functions of the adsorption potential (see Eq. (*3*)), calculated from the Dubinin–Radushkevich equation for H(95).NaY coked at different temperatures. ——— 523 K, ······ 573 K, ----- 593 K, — — — 623 K, —·—·— 673 K. The top curve is for the parent sample

CONCLUSIONS

The conclusions can be summarized as follows: The effect of temperature on the rate of forming coke deposits was confirmed. The temperature influences the kinetics of the formation as well as the ratio of external to internal coke. XRD and IR results show that noticeable process of coke formation in the system under study occurs at temperatures above 473 K. The ratio of polyaromatic to aliphatic compounds in the deposits increases with coking temperature. At elevated temperatures, diffusion to and detachment from the zeolite-crystal surface of some coke deposits probably occur. There is a possibility of controlled deposition of coke, so that, depending on need, adsorbents of definite sorption properties can be obtained.

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